

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
29 March 2001 (29.03.2001)

PCT

(10) International Publication Number  
**WO 01/21680 A1**

- (51) International Patent Classification<sup>7</sup>: C08G 63/80, 63/88, B29C 49/00, C08K 3/08 (72) Inventor: HARRISON, David, Anthony; 17 Shoreham Close, Redcar, Cleveland TS10 2RD (GB).
- (21) International Application Number: PCT/US00/25858 (74) Agent: KRUKIEL, Charles, E.; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).
- (22) International Filing Date:  
21 September 2000 (21.09.2000) (81) Designated States (*national*): BR, CA, CN, ID, IN, JP, KR, MX, SG, TR, VN, ZA.
- (25) Filing Language: English (84) Designated States (*regional*): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
- (26) Publication Language: English
- (30) Priority Data:  
09/400,027 21 September 1999 (21.09.1999) US Published:  
— With international search report.
- (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).  
*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*



WO 01/21680 A1

(54) Title: METHOD FOR ADJUSTING REHEAT PROPERTIES OF POLYESTER RESINS

(57) Abstract: A method for precisely adjusting the reheat properties of a polyester resin containing finely divided particles of antimony as IR-absorbant over a wide range without having to materially change the resin composition by contacting the polyester resin in the solid state in the presence of a heated inert gas with an amount of oxygen.

TITLE  
METHOD FOR ADJUSTING REHEAT PROPERTIES  
OF POLYESTER RESINS  
BACKGROUND OF THE INVENTION

5       The present invention relates to a process for preparing polyester resins which exhibit desirable reheat properties, and, more particularly, the present invention relates to a method for precisely adjusting the reheat properties of a polyester resin over a wide range without having to materially change the resin composition.

10       U.S. Patent Nos. 5,419,936 and 5,529,744 describe a method for reducing the reheat time of polyester resins by introducing between 3 parts per million (ppm) and 300 ppm by weight of fine metal particles into the resin matrix during synthesis. The metal particles are selected based on their ability to intrinsically absorb radiation in the wavelength region 500 nm to 2000 nm, which is the  
15       wavelength region emitted by most commercially available quartz infra-red lamps used for reheat purposes. The metal particles are sufficiently fine for them not to be visible to the eye, and they have a range of sizes such that absorption of radiation can occur over a relatively wide part of the wavelength range.

      The amount of metal particles present in the resin composition as it is to be  
20       used in forming bottles from bottle preforms is a balance between the desired reduction in reheat time for the polymer, i.e., the preform, and the amount of haze that is acceptable in a given end use. The concentration of contaminants, e.g., metal particles, can contribute to an unacceptably high haze level. It has been found that antimony metal particles at concentrations of from 3 ppm to 300 ppm  
25       can produce satisfactory reheat times for poly(ethylene terephthalate) [PET] compositions.

      In practice, the antimony metal particles are derived from antimony trioxide (antimony (III) oxide), i.e., a reducible form of antimony, and the PET polymer includes a suitable reducing agent. Reaction between the metal  
30       compound and the reducing agent during processing of the polymer leads to formation of the metal distributed generally throughout the polymer. The quantity of reducing agent to be used must be determined by experimentation and operating experience.

      A problem exists, however, in not being able to produce a PET resin  
35       according to a set base recipe but also capable of having a range of reheat characteristics. According to the present invention, it is now possible to produce a fast reheat PET resin from a base recipe, which resin is also capable of having a

range of reheat characteristics, by controlling one parameter during the solid state processing stage for the resin.

### SUMMARY OF THE INVENTION

The present invention is an improvement in a continuous process for producing a PET resin from a PET prepolymer which contains a concentration of finely divided antimony metal particles. The process comprises introducing the PET prepolymer into a moving bed reaction zone while contacting the prepolymer within the reaction zone with a heated inert gas. The improvement according to the invention comprises simultaneously introducing into the reaction zone and contacting the PET prepolymer with a predetermined concentration of oxygen in the range of from 10 ppm up to 350 ppm, based on the volume of inert gas, whereby to selectively convert a portion of the finely divided antimony particles to antimony trioxide.

According to another aspect, the invention is a method for adjusting the reheat rate of a solid state polymerized linear polyester, e.g., PET, which contains a beginning concentration of finely divided antimony particles. The method comprises contacting the linear polyester in the solid state in the presence of a heated inert gas with an amount of oxygen in the range of from 10 to 350 parts per million, based on the volume of inert gas, whereby a predetermined portion of the beginning concentration of antimony is converted to antimony trioxide.

The selection of oxygen level allows for the production of a PET composition having a range of reheat rates without changing the recipe, i.e., the specification, of the polymer composition.

The practice of adjusting of the reheat rate of the polymer by changing a single easily controlled parameter in the solid phase portion of the process is much simpler to carry out than changing the prepolymer composition. In continuous process methods of production, the invention reduces the amount of intermediate reheat material that is normally produced when changing from one reheat grade of resin to another because the prepolymer composition can remain unchanged.

### DETAILED DESCRIPTION

The present invention resides in the discovery that it is possible to control the infra-red absorption properties of commercially produced PET resins which contain finely divided antimony metal particles by exposing the PET prepolymer to controlled levels of oxygen during the solid-state polymerization stage of the production process.

PET is produced on a continuous basis at commercial rates by reacting a glycol with a dicarboxylic acid, as the free acid or its dimethyl ester, to produce a prepolymer compound which is then polycondensed to produce the polyester. A

reducible antimony metal compound, usually in the form of antimony trioxide, is incorporated into the prepolymer with a suitable reducing agent during synthesis, i.e., in the melt phase, so that reaction between the metal compound and the reducing agent during processing of the polymer melt leads to formation of the metal which is distributed throughout the prepolymer. The object of the process is to add only sufficient reducing agent to reduce only a proportion of the antimony trioxide such that the antimony metal concentration thereby produced imparts the desired level of reheat to the resin. Complete reduction of all the antimony trioxide leads to a resin which is too dark and which does not have satisfactory color for use in PET bottles. In practice, the degree of reduction and hence the proportion of the antimony trioxide that is converted to antimony metal particles, is a complex function of the oligomeric composition of the prepolymer, reducing agent concentration and point at which the reducing agent is added to the prepolymer. It follows that the prepolymer composition which leads to a specific reheat rate for the final polymer is unique for each route of manufacture. The composition must therefore be carefully formulated for each individual process, such as in the illustration given in Example 2 below.

After the melt polymerization process, the molecular weight of the prepolymer, which is typically in the range of from 0.55 to 0.65 dl/g, is further increased by solid state polymerization to a value typically in the range of from 0.75 to 0.85 dl/g as required for commercial application.

The prepolymer is first crystallized in one or more stages at temperatures in the range 120° to 180°C in either air or an inert atmosphere. At the outset the resin is heated in an agitated reactor to prevent the amorphous chip from sticking before it has crystallized. Secondary crystallization stages may then be employed to raise the crystallinity of the resin to the desired level prior to the reaction stage of the process. In the reaction stage the precrystallized prepolymer is processed in one or more moving bed reactors at higher temperatures, typically in the range of from 200°-230°C, in an atmosphere of hot inert gas in order to raise the molecular weight of the final polymer to the desired level. In a typical solid state polymerization process the inert gas used is nitrogen. Oxygen levels in the nitrogen stream are normally maintained at the lowest possible levels during this stage to minimize the problem of oxidative degradation, which can restrict the rate at which the polymerization reaction proceeds and lead to color formation (e.g., yellowing) in the resin.

According to the invention, it is now possible to employ a single recipe for the PET prepolymer composition which contains an excess of antimony metal, yet have the capability to produce a wide range of reheat grades of resin without

having to change the polymer recipe by controlling the oxygen level at precise, higher than normal levels during the solid state polymerization process. The oxygen level in the inert gas used in the solid state polymerization step can be set at any predetermined value over a range of from 10 ppm up to 350 ppm whereby the desired concentration of antimony metal is oxidized. Re-oxidized antimony particles, i.e., those which are converted to antimony trioxide, do not absorb infra-red radiation. Exposure of the prepolymer to as little as 10 ppm of oxygen during solid state polymerization has produced a measurable effect in terms of reheat time.

The invention will now be illustrated by reference to the following examples.

### EXAMPLE 1

#### Laboratory Scale

A 1 kilogram sample quantity of "fast reheat" amorphous base PET prepolymer chip was crystallized by heating for 4 hours in an air oven at 130°C.

The 1 kilogram sample of crystallized chip was then heated as a static column in a glass tube with a porous sintered glass base, through which heated nitrogen as the inert gas was passed at a flow rate of 40 liters/min in order to polymerize the chip in the solid state. The nitrogen was heated by first being passed through a glass coil inside a glass vapor bath jacket containing a boiling liquid with the same boiling point as the required solid state polymerization reaction temperature. The oxygen level in the nitrogen was precisely controlled by feeding gas from a 200 bar ( $20 \times 10^3$  kPa) cylinder of "Beta standard" purity 5% oxygen in nitrogen (Air Products) into a pure nitrogen stream via precisely calibrated flowmeters to give an inert gas/oxygen mixture with the desired level of oxygen.

The chip was heated in this way, at selected temperatures and selected oxygen levels, for between 4 and 8 hours. For purposes of this laboratory example, the temperatures used were between 192°C and 215°C, and the oxygen amounts added to the nitrogen stream were between 10 and 350 parts per million.

The final polymerized polymers were injection molded into 10 cm diameter x 4 mm thick circular plaques on which reheat, infra-red absorption, color and haze was measured. Reheat was measured on a scale of values based on a standard preform reheat test (E. I. du Pont de Nemours and Company, Standard Test Method for Minimum Blowing Time Test No. MST 116). The test compares the minimum blowing time required to produce a clear PET bottle. The blowing time required for a test sample is compared with that for a "zero seconds reheat" standard polymer. The difference is quoted as the "reheat" of the test sample.

The reheat values observed at different oxygen levels at a solid state polymerization temperature of 215°C are shown in the table below.

Oxygen in nitrogen stream / ppm	Reheat time / seconds
0	- 9.0
10	- 7.3
20	- 6.4
30	- 6.4
40	- 6.2
100	- 4.1
200	- 3.4
350	- 2.1

5 It can be seen that increasing the oxygen level in the gas stream has the effect of increasing the reheat time that is required, such that it approaches the reheat time required for the “zero seconds” reheat reference sample upon which the reheat test is based - that is, the reheat capacity is reduced with increasing oxygen level.

10 A relationship between the reheat rate and oxygen levels between 10 and 350 parts per million during solid state polymerization has therefore been demonstrated.

### EXAMPLE 2

#### Commercial Plant Scale

15 Amorphous base polymer with the desired composition was produced by a commercial continuous melt process in which terephthalic acid and ethylene glycol were reacted in three separate stages.

The first was the esterification stage in an “Esterifier” vessel, in which terephthalic acid and ethylene glycol in the form of a slurry of molar ratio of about  
20 2 to 1 reacted to form monomer, low molecular oligomer and water. This was carried out at 280°-290°C and atmospheric pressure, during which excess glycol and the water produced during the reaction were distilled off.

The monomer and oligomer was continuously fed to the second part of the process, the pre-polymerization stage in the “Upflow Pre-polymerizer” (UFPP).  
25 Here the oligomer was reacted under intermediate vacuum at 280°-295°C to increase the degree of polymerization of the oligomer to produce the “pre-polymer”. Low pressure in the UFPP removed excess glycol and glycol generated during the polymerization reaction.

30 In the transfer line between the Esterifier and the UFPP catalysts, color modifiers and stabilizer compounds were injected into the monomer/oligomer.

Firstly, phosphoric acid ( $\text{H}_3\text{PO}_4$ ) and phosphorous acid ( $\text{H}_3\text{PO}_3$ ) stabilizers, both at levels of 80 ppm in the final polymer, were injected in the form of solutions in diethylene glycol. Secondly, cobalt acetate color modifier (160 ppm) and antimony trioxide polycondensation catalyst (270 ppm) were added in the form of solutions in ethylene glycol.

The molten prepolymer was continuously fed from the UFPP to the third and final stage, the "Finisher", in which the prepolymer was reacted to form an intermediate molecular weight polymer under high vacuum at  $285^\circ\text{--}300^\circ\text{C}$ . The vessel contained a wiped-wall agitator which drives the highly viscous polymer melt through the vessel. The vacuum removed glycol generated during the polymerization reaction. The molten polymer finally passed through filters before being extruded through die-heads to form laces which were quenched and then chopped into chips. The polymer had an intrinsic viscosity (IV) of 0.58-0.62 dl/g.

The amorphous base chip was then solid state polymerized in a continuous commercial production plant process to raise the viscosity to the desired level of the final product. The process involved subjecting the intermediate MW polymer to a precrystallization stage, a crystallization stage, a preheating stage and a final solid state polymerization stage, in which the chip passed from stage to stage in a continuous flow with a throughput of between 10 and 15 tons of product per hour.

In the first stage the amorphous polymer was precrystallized by heating it at a temperature of  $160^\circ\text{C}$  for about 20 minutes in an air atmosphere in a fluidized reactor vessel with an inventory of about 4 tons of material.

In the second stage the crystallinity of the chip was raised by heating the chip to a temperature of about  $175^\circ\text{C}$  for between 5 and 10 minutes in an air atmosphere in a second fluidized reactor with an inventory of 1 to 2 tons.

In the third stage the IV and temperature of the chip was raised further by heating the chip to a temperature of about  $215^\circ\text{C}$  and holding it for 4 hours in a plug-flow "preheater" vessel under a recirculated nitrogen atmosphere and an inventory of 70 tons of material. In this stage the IV was raised from about 0.58-0.62 dl/g to about 0.68 dl/g.

In the fourth and final stage the chip was heated in a vertical plug-flow solid state polymerization reactor at  $205^\circ\text{C}$  to  $210^\circ\text{C}$  and held at that temperature for about 15 hours in a recirculating nitrogen atmosphere and an inventory of about 150 tons of polymer in order to achieve the desired final intrinsic viscosity. In this stage the IV was raised from about 0.68 dl/g to about 0.82 dl/g.

The nitrogen stream was recirculated through the preheater to the solid state polymerization reactor and then back to the preheater via firstly a platinum bed catalyst "regeneration" unit in which oxygen and organic rich off-gases in the

gas stream were combusted to CO<sub>2</sub>, and secondly via a dehumidification unit containing a molecular sieve desiccant material to remove moisture from the gas stream. The regeneration and dehumidification units were located between the preheater and the solid state polymerization reactor. The regeneration process was controlled by feeding a small and precisely controlled excess quantity of oxygen into the unit to ensure adequate combustion. An oxygen level meter of the "Orbisphere" type was located between the regeneration and dehumidification units. Measurements from this meter were continuously taken and, via a feedback loop, used to automatically control the valve which inputs the excess oxygen to the combustion process such that consistent oxygen levels were maintained in the gas stream.

For normal production the oxygen in the recirculated gas stream is precisely controlled at 16-20 parts per million. At this oxygen level the prepolymer composition described above leads to a final polymer with a reheat of minus 12 to minus 14 seconds according to the MST 116 preform reheat scale.

For the purposes of this invention, the level of oxygen in the nitrogen stream was deliberately increased by adjusting the control loop between the oxygen meter to supply less excess oxygen input to the regeneration unit. In this way less combustion took place and hence the resulting oxygen level in the gas stream could be increased and precisely controlled.

190 ppm oxygen was found to give a final product with a significantly reduced reheat, minus 4 to minus 6 seconds, with the same prepolymer composition. The product can be used in applications in which faster reheat is not a necessity and offers no commercial advantage. Furthermore the polymer has lower haze and a lighter color than the faster reheat product, both of which are of commercial advantage in some applications.

In a conventional process, adjustment of the reheat of the final product would normally be carried out by changing the phosphorous and phosphoric acid levels injected into the oligomer. On this scale of production this leads to a considerable quantity of material produced at intermediate and undesirable reheat due to the long time needed for the new formulation to come through as a final product. The quantity of intermediate material produced in the novel process in this example according to the invention was greatly reduced.

Any reheat between the values derived from the oxygen levels described above could be produced simply by selecting the required intermediate oxygen level.

The above examples do not limit the scope of the invention to the type of melt, solid phase polymerization process or oxygen level control procedure which

can be used. Any process in which polymer chip containing antimony metal particles is deliberately exposed to oxygen levels in the range described during solid state polymerization will undergo re-oxidation of these particles and hence a reduction in its reheat capacity.

WHAT IS CLAIMED IS:

1. In a process for the continuous solid state polymerization of crystalline linear polyester prepolymer which contains a beginning concentration of finely divided particles of antimony which process comprises introducing the crystalline linear polyester prepolymer into a moving bed reaction zone and contacting said polyester prepolymer within the reaction zone with a heated inert gas, the improvement comprising simultaneously contacting said polyester prepolymer with a predetermined concentration of oxygen in the range of from 10 ppm up to 350 ppm, based on the volume of inert gas, whereby a portion of the beginning concentration of antimony is converted to antimony trioxide.
2. A method for adjusting the reheat rate of a solid state polymerized linear polyester polymer which contains a beginning concentration of finely divided antimony particles, said method comprising contacting said polyester in the solid state in the presence of a heated inert gas with an amount of oxygen in the range of from 10 ppm to 350 ppm, based on the volume of inert gas, whereby a portion of the beginning concentration of antimony is converted to antimony trioxide.
3. A method for controlling infra red radiation absorption by a polyester resin which contains a beginning concentration of finely divided infra red radiation absorbing antimony particles which comprises contacting said polyester in the solid state in the presence of a heated inert gas with an amount of oxygen in the range of from 10 ppm to 350 ppm, based on the volume of inert gas, whereby a portion of the beginning concentration of antimony is converted to antimony trioxide.

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G63/80 C08G63/88 B29C49/00 C08K3/08

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G B29C C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, CHEM ABS Data, EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 429 311 A (ICI PLC) 29 May 1991 (1991-05-29) claims 1,6-8; example 1 & US 5 419 936 A 30 May 1995 (1995-05-30) cited in the application ---	1-3
Y	US 3 497 477 A (BARKEY KENNETH T ET AL) 24 February 1970 (1970-02-24) claim 1 column 3, line 54 -column 5, line 38 column 11, line 36 - line 44 ---	1-3
A	EP 0 693 356 A (ICI PLC) 24 January 1996 (1996-01-24) abstract; example 1 -----	1-3

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

\*A\* document defining the general state of the art which is not considered to be of particular relevance

\*E\* earlier document but published on or after the international filing date

\*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

\*O\* document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*&amp;\* document member of the same patent family

Date of the actual completion of the international search

21 December 2000

Date of mailing of the international search report

04/01/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Krische, D

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0429311 A	29-05-1991	AT 162206 T	15-01-1998
		BR 9005938 A	24-09-1991
		CA 2030668 A	25-05-1991
		CN 1051922 A,B	05-06-1991
		CN 1131609 A,B	25-09-1996
		CN 1130564 A,B	11-09-1996
		DE 69031937 D	19-02-1998
		DE 69031937 T	30-04-1998
		DK 429311 T	07-09-1998
		ES 2111532 T	16-03-1998
		GR 3025994 T	30-04-1998
		JP 3230933 A	14-10-1991
		KR 170389 B	30-03-1999
		MW 8990 A	08-01-1992
		TR 28654 A	17-12-1996
		US 5419936 A	30-05-1995
		US 5529744 A	25-06-1996
		ZA 9009312 A	29-04-1992
		ZA 9109312 A	25-11-1992
		ZM 5290 A	30-08-1991
		ZW 18390 A	02-10-1991
US 3497477 A	24-02-1970	NONE	
EP 0693356 A	24-01-1996	AT 147676 T	15-02-1997
		BR 9102471 A	21-01-1992
		CA 2044683 A	16-12-1991
		CN 1059503 A,B	18-03-1992
		CN 1105681 A,B	26-07-1995
		DE 69124151 D	27-02-1997
		DE 69124151 T	24-04-1997
		DK 465040 T	14-07-1997
		EP 0465040 A	08-01-1992
		ES 2095912 T	01-03-1997
		GR 3022296 T	30-04-1997
		JP 4232722 A	21-08-1992
		MW 2191 A	12-02-1992
		US 5409983 A	25-04-1995
		ZA 9104589 A	25-03-1992
		ZM 2391 A	27-03-1992
		ZW 7291 A	11-03-1992